

## *Letters to the Editor*

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### FLUCTUATIONS AND THERMAL CONDUCTIVITY OF CO<sub>2</sub> IN THE CRITICAL REGION

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The measurement of the thermal conductivity of CO<sub>2</sub> in the critical region has recently been receiving considerable attention (Guildner 1958; Michels *et al.*, 1962b). The most interesting feature of these measurements is the appearance of a sharp maximum in the thermal conductivity vs. density curve near the critical density. It has been observed (Michels and Strijland 1952) that the specific heat of CO<sub>2</sub> also shows a similar behaviour in the critical region. This has led Michels *et al.* (1962c) to suggest that the variation of thermal conductivity in the critical region is in some way connected to the variation of specific heat in that region. They have also suggested that due to the formation and the breaking up of the clusters in the critical region additional heat may be transferred as observed in dissociating systems (Hirschfelder 1957, Butler and Brokaw, 1957). The problem of heat transfer in the critical region has been treated along these lines by Barua and Das Gupta (1966) without much success. It, however, appears that a factor which has not yet been considered for explaining the thermal conductivity is the fluctuations in the critical region. Recently, Fixman (1965) has explained the heat capacity of CO<sub>2</sub> in the critical region fairly well by considering density fluctuations given by

$$\langle (\delta n)^2 \rangle = \int \langle n_k n_{k'} \rangle \exp [i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{R}] d\mathbf{k} d\mathbf{k}' \quad (1)$$

where the symbols have their usual meanings.

Michels and Sengers (1962a) made several tests to find whether there was any significant convection effect in their measurement of the thermal conductivity of CO<sub>2</sub> in the critical region. The most important of these tests is the variation

of the temperature difference  $\Delta T$  between the hot and the cold plates of conductivity cell. From the lack of variation of the measured thermal conductivity with  $\Delta T$ , they concluded that their measurements were convection-free. However, density fluctuations in the critical region are not dependent on  $\Delta T$ . Consequently the convection due to this factor will not change effectively with  $\Delta T$ . This means that convection due to density fluctuations is an inherent property of the critical region which cannot be avoided by any modification of the apparatus for thermal conductivity measurement. This effect will be maximum at the critical point as the density fluctuation is also maximum at that point. Very recently an experiment on convection near the critical region has been performed by Hahne (1965). He has observed a very large increase of heat transfer at the critical region which may at least be partially due to density fluctuations.

At present we have no theoretical treatment to calculate the effect of convection due to density fluctuations on the thermal conductivity measurement near the critical region. It is quite possible when this convection effect is accounted for the observed maximum in the thermal conductivity vs. density curve for  $\text{CO}_2$  may disappear.

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